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Short communication

Co-sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium ion battery

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HIGHLIGHTS

- The sintering temperature of garnet electrolyte was found to significantly lower by addition.
- The simultaneous interdiffusion of elements was important to lower sintering temperature.
- Garnet oxide exhibited high lithium ion conductivity despite of the low sintering temperature.
- All-solid-state lithium ion battery using garnet oxide was fabricated by co-sintering.

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ABSTRACT

We investigated the development of a novel lithium garnet-type oxide electrolyte, which is co-sinterable with a metal oxide cathode, for practical all-solid-state lithium ion batteries using metal oxide electrolytes. The sintering temperature of $Li_{6.8}(La_{2.95},Ca_{0.05})(Zr_{1.75},Nb_{0.25})O_{12}$ was found to significantly lower to 790 °C by addition of Li_3BO_3 and Al_2O_3, due to simultaneous interdiffusion of Al and Ca elements between garnet-type oxide and additives. The sintered electrolyte exhibited high lithium ion conductivity of 0.36 mS cm^{-1} at 25 °C despite of the low sintering temperature. An all-solid-state lithium ion battery was successfully prepared by co-sintering of the electrolyte and $LiCoO_2$ (cathode), followed by coating of Li metal (anode), and confirmed to function well as a secondary battery with charge and discharge capacities of 98 and 78 mAh g^{-1}, respectively. These results opened the potential for fabrication of all-solid-state lithium ion batteries by a simple and well-established co-sintering process.

1. Introduction

Lithium ion secondary batteries have been widely used as power sources for electric vehicle (EV), a mobile phone and etc., and are now indispensable for our daily lives. At the same time, safety of the batteries has been becoming an important issue with the progress of their performance (e.g. capacity and energy density). From this viewpoint, all-solid-state lithium ion batteries using solid electrolytes have attracted much attention as a next-generation battery due to non-use of flammable organic liquid electrolytes.

Especially, specific focus has been place on “metal oxide” electrolytes rather than others (e.g. sulfide electrolyte) because metal oxides are stable in air and thus never release toxic gases even in case of breaking down. In addition, metal oxide electrolyte has several advantages such as high chemical and thermal stability and a low charge transfer resistance between the electrode/electrolyte interfaces [1–3]. Furthermore, metal oxide electrolyte/electrode systems have a great merit to construct a bi-polar structure for high capacity, because a layer-by-layer structure of electrolyte, electrode and metal is easily fabricated by a simple co-sintering process, which has been widely used in production of multi-layered ceramic capacitors. However, low lithium ion conductivities of metal oxide electrolytes (e.g. 1 μS cm^{-1} at R.T.) limited their use for all-solid-state batteries.

The important breakthrough in this field was achieved in 2007 by R. Murugan, who first reported $Li_7La_3Zr_2O_{12}$ (LLZO) and its derivatives with high lithium ion conductivity (~0.1 mS cm^{-1} at R.T.) [4–13]. The discovery motivated researches on the use of metal oxide electrolytes for all-solid-state batteries. We also investigated the electrochemical performance of a model battery using an as-sintered Nb doped LLZO (LLZO-Nb, 0.8 mS cm^{-1} at 25 °C) pellet and $LiCoO_2$ (LCO, one of typical cathodes), and found that the model battery exhibited good charge–discharge capacities and low interfacial resistance between LCO and LLZO-Nb comparable with

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that of lithium ion batteries with liquid organic electrolytes [2,14]. The results confirmed the availability of LLZO-Nb as a metal oxide electrolyte for all-solid-state batteries. The next challenge is co-sintering of electrolyte and electrode materials with high densities but without the formation of other compounds by interdiffusion.

Here, we investigated the design of LLZO-Nb for co-sintering with LCO (cathode) for the first step because it is one of the most important issues to suppress the reaction of LLZO-Nb and cathode by drastically lowering the sintering temperature of LLZO-Nb to less than 900 °C [15]. In order to overcome this difficulty, our strategy is to enhance interdiffusion between LLNO-Nb and a grain boundary phase (not LCO) by an appropriate selection of additives. As the result, addition of Al_2O_3 and Li_3BO_3 to Ca and Nb doped LLZO (LLZO-CaNb) lowered the sintering temperature to 790 °C with maintaining high lithium ion conductivity but without the reaction with LCO. The developed electrolyte pellet was stacked on a LCO (cathode) pellet, co-sintered at 790 °C and coated with Li metal (anode). The obtained model battery was confirmed to work properly with charge–discharge capacities of 72% and 58%, respectively, to the theoretical value. The present results opened the potential to produce all-solid-state lithium ion battery by a simple co-sintering process.

2. Experimental

Commercial reagents were purchased from Sigma–Aldrich and Kojundo Chemical Lab. Co. Ltd. and used as received for Li(OH), $La(OH)_3$, $Ca(OH)_2$, ZrO_2, Nb_2O_5, Li_2CO_3, B_2O_3 and γ-Al_2O_3. LLZO-CaNb was prepared by conventional solid state reactions. The starting materials, Li(OH), $La(OH)_3$, $Ca(OH)_2$, ZrO_2, and Nb_2O_5 were mixed by planetary ball-milling, and then calcined at 700 °C for 48 h. The composition of the samples were evaluated by inductively coupled plasma spectroscopy (ICP:Rigaku Co. CIRIOS 120 EOP). Li_3BO_3 powder as an additive was prepared by heating a mixture of Li_2CO_3 and B_2O_3 at 600 °C. The calcined LLZO-CaNb powder was mixed with the additives (both Al_2O_3 and Li_3BO_3, only Al_2O_3 or only Li_3BO_3) by planetary ball-milling. The mixture was die-pressed at 10 MPa into a pellet (green density: ca. 40% (2.10 g cm^{-3})) and sintered at 790 °C for 40 h in air. The crystal structure and the lattice parameter of the samples were evaluated by X-ray diffraction (XRD:Rigaku Co. Ultima IV, CuKα radiation, 40 kV, 30 mA). The electrical conductivity of the samples was measured using a two-probe AC impedance method (Agilent 4294A) in the frequency range of 110 MHz–40 Hz from 25 to 150 °C. The distribution of the elements was measured by EPMA (JEOL Ltd. JXA-8500F). The cathode/electrolyte stacked pellet was prepared by co-sintering process. A commercial $LiCoO_2$ powder (average particle size: 5 μm, Nippon Chemical Industrial Co., Ltd.) as a cathode was mixed with Li_3BO_3 and the calcined LLZO-CaNb powder in the ratio of 42:35:23 (wt%). The mixed powder was put on the LLZO-CaNb electrolyte pellet and co-die-pressed at 10 MPa. The stacked pellet was sintered at 790 °C in air. The morphology and the elemental distribution of the cathode/electrolyte interface were observed by FIB-SEM (Hitachi NB5000 FIB-SEM, 5 kV) and EDX (EDAX Inc. GenesisAPEX2), respectively. The charge–discharge curves were obtained using a potentio galvanostat (Solartron 1480) under galvanostatic conditions of 1 μA g^{-1} (rate: ~0.01C) in the range from 3.0 to 4.2 V.

3. Results and discussions

$Li_{6.8}(La_{2.95},Ca_{0.05})(Zr_{1.75},Nb_{0.25})O_{12}$ (LLZO-CaNb) was chosen as the base garnet-type oxide compound due to its high lithium ion conductivity (~0.6 mS cm^{-1} at 25 °C) and lower sintering temperature (1050 °C) than those of other lithium garnet-type oxides [16]. The composition ratio of Li/La/Ca/Zr/Nb in calcinated LLZO-CaNb powder which was evaluated by ICP was 6.81/2.96/0.05/1.75/0.25, where this ratio was normalized according to Zr at 1.75. Al_2O_3 and Li_3BO_3 were selected as additives for lowering the sintering temperature due to the following reasons. The Al^{3+} ion can be substituted to the Li^+ site in LLZO-CaNb by interdiffusion into the LLZO-CaNb grain, which can improve the sinterability of LLZO-CaNb. The Al^{3+} ion was added until its solubility limit (0.2 mol %) to LLZO-CaNb [17–19]. Li_3BO_3 can form a liquid phase due to its low melting point (ca. 700 °C) and thus enhance liquid phase sintering of LLZO-CaNb without reactions with it [20]. The effects of Li_3BO_3 addition on sinterability and lithium ion conductivity were preliminarily evaluated for LLZO-CaNb with Al_2O_3 (0.2 mol%) is shown in Fig. 1. The addition of ≥5 vol.% was effective for densification, whereas the addition of >10 vol.% resulted in the decrease of the lithium ion conductivity due to the large increase of the grain boundary resistance. This can be explained by the mechanism that Li_3BO_3 tends to exist at the grain boundaries in addition to the triple points, which leads to insufficient contact between LLZO-CaNb grains. Thus, the amount of Li_3BO_3 addition was determined as 5–10 vol.% to LLZO-CaNb according to these results.

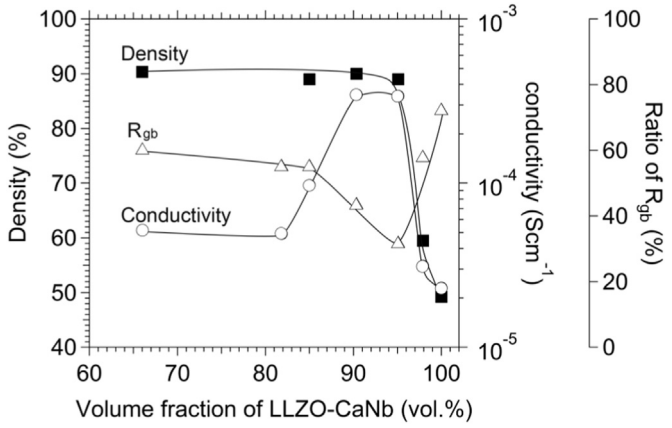

Fig. 1. Effects of Li_3BO_3 addition on density (square), lithium ion conductivity (open circle) and the ratio of resistance due to grain boundary (open triangle) for LLZO-CaNb with Al_2O_3 (0.2 mol%).

Sinterability of LLZO-CaNb was drastically improved by co-addition of Al_2O_3 and Li_3BO_3. Table 1 lists the relative densities for die-pressed pellets of a calcined LLZO-CaNb powder with or without the additives (both Al_2O_3 and Li_3BO_3, only Al_2O_3, only Li_3BO_3 and no additives) after sintering at 790 °C in air. It is clear that (i) the formation of a liquid phase (addition of Li_3BO_3) is effective for densification of LLZO-CaNb and (ii) the relative density increases up to nearly 90% only in the case of co-addition of Al_2O_3 and Li_3BO_3. The XRD pattern of all the diffraction peaks confirmed the formation of a cubic garnet type structure (space group: *I*a-3d, JCPDS: 84-1753) with the lattice parameter of 12.95 Å (Fig. 2). The ICP analysis showed that the composition ratio of Li/La/Ca/Zr/Nb/

Table 1
Relative density and lithium ion conductivity of the samples.

Base	Additive	Rel. dens. (%)[a]	Li^+ σ (mS cm^{-1})
LLZO-CaNb	Al_2O_3, Li_3BO_3	90	0.36
LLZO-CaNb	–	49	0.004
LLZO-CaNb	Al_2O_3	49	0.008
LLZO-CaNb	Li_3BO_3	52	0.006

[a] The theoretical density was calculated based on the ideal densities of LLZO-CaNb (5.08 g cm^{-3}) and LBO (2.16 g cm^{-3}) and their mixing ratio (90/10) in volume.

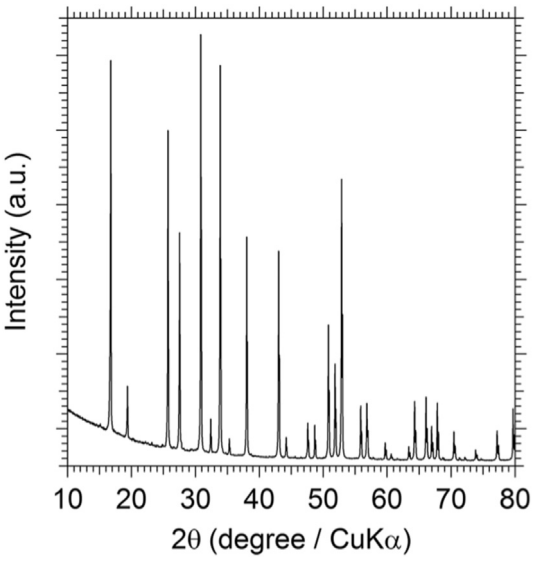

Fig. 2. XRD pattern of LLZO-CaNb with co-addition of Al_2O_3 and Li_3BO_3 sintered at 790 °C.

Al/B in sintered LLZO-CaNb with co-addition of Al_2O_3 and Li_3BO_3 was 7.55/2.95/0.31/1.75/0.25/0.19/0.22, normalized according to Zr at 1.75.

Electron probe microanalysis (EPMA) was conducted in order to unravel the mechanism of the improvement of the sinterability by co-addition of Al_2O_3 and Li_3BO_3 (Fig. 3). It is of interest that (i) the Al element is homogeneously distributed in the LLZO-based grains whereas (ii) the Ca and B elements are located in the triple points [21]. The results indicate that the Al element, initially located out of the LLZO-CaNb crystals, diffuses into the LLZO-based grains while the Ca element, initially located in the LLZO-CaNb crystals, diffuses into the Li_3BO_3-based triple points during sintering, as shown as the following chemical equation.

$$\text{LLZO-CaNb} + Al_2O_3 + Li_3BO_3 \rightarrow \text{LLZO-AlNb} + \text{Li–Ca–B–O} \quad (1)$$

Table 2
Relative density and lithium ion conductivity of the samples.

Base	Additive	Rel. dens. (%)[a]	Li^+ σ (mS cm^{-1})
LLZO-AlNb	CaO, Li_3BO_3	76	0.09
LLZO-Nb	Al_2O_3, Li_3BO_3	72	0.08

[a] The theoretical density was calculated based on the ideal densities of LLZO-CaNb (5.08 g cm^{-3}) and LBO (2.16 g cm^{-3}) and their mixing ratio (90/10) in volume.

The simultaneous interdiffusion between the garnet-type oxide and the additives in addition to the formation of a liquid phase is considered to significantly improve the sinterability of LLZO-CaNb. The importance of the simultaneous interdiffusion during sintering was further confirmed by two additional experiments. Table 2 lists the relative densities and lithium ion conductivity of the sintered sample for the LLZO-Nb (based garnet-type oxide)/(CaO and Li_3BO_3) (additives) and LLZO-Nb based garnet-type oxide)/(CaO and Li_3BO_3) (additives) after sintering at 790 °C. The relative density of the sintered sample was 76% for the LLZO-AlNb (base garnet-type oxide)/(CaO and Li_3BO_3) (additives) system, which suggests that the simultaneous interdiffusion rather than the final compositions of the grain and the triple points is crucial for the densification. In addition, the density of the sintered sample was 72% for the LLZO-Nb (base garnet-type oxide)/(Al_2O_3 and Li_3BO_3) (additives) system, which suggests that the diffusion of both the Al and Ca elements are necessary for the densification.

The developed LLZO-AlNb in this study was confirmed to exhibit high lithium ion conductivity (0.36 mS cm^{-1} at R.T.), comparable to those of LLZO-based materials sintered at high temperature (1000–1200 °C), despite of the low sintering temperature of 790 °C. Fig. 4a shows the Nyquist plots at 25 °C for the developed LLZO-AlNb and LLZO-AlNb prepared by a conventional process (sintered at 1150 °C, abbreviated as LLZO-AlNb-conv.). Two semicircles at higher and lower frequencies, which were observed in both samples, are assigned to the bulk resistance (R_b) and the grain boundary resistance (R_{gb}), respectively [9]. The R_b was 2.1 and 2.0 kΩ cm and the R_{gb} was 0.53 and 0.48 kΩ cm for the developed LLZO-AlNb and LLZO-AlNb-conv., respectively. The calculated lithium ion conductivity of the developed LLZO-AlNb (0.36 mS cm^{-1}) was almost same

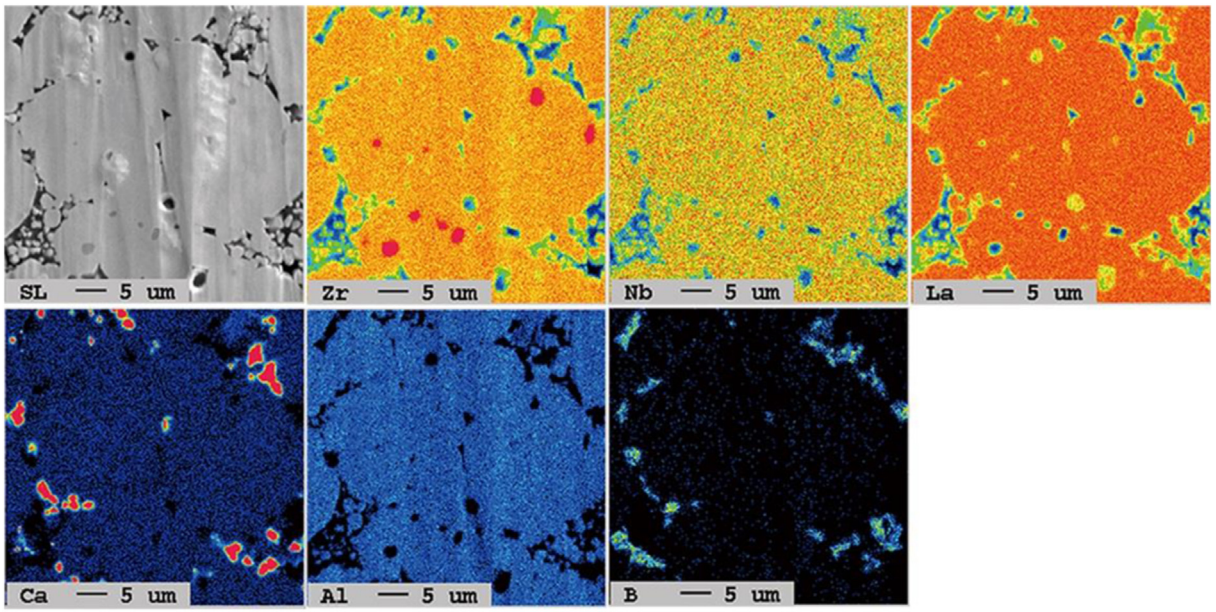

Fig. 3. Cross-sectional EPMA mapping images of LLZO-CaNb with co-addition of Al_2O_3 and Li_3BO_3 sintered at 790 °C.

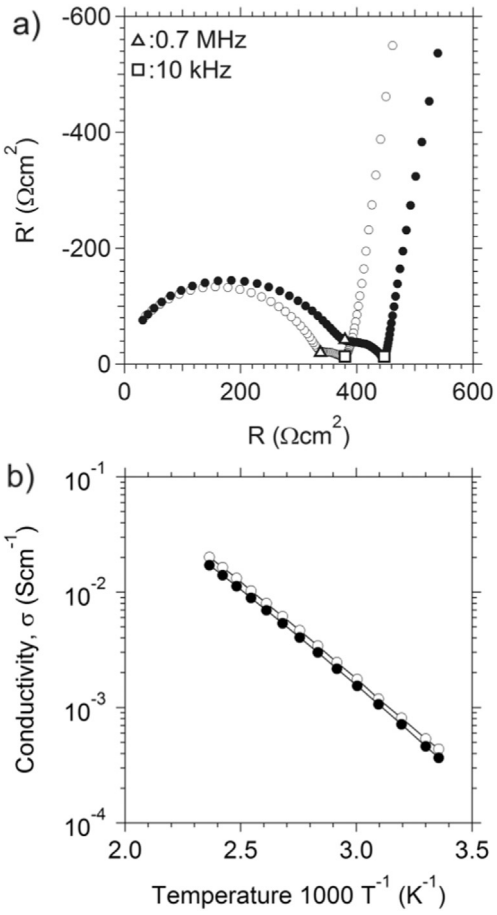

Fig. 4. a) Nyquist plots (110 MHz–40 Hz) of the developed LLZO-AlNb (solid circle) and LLZO-AlNb prepared by a conventional process (sintered at 1150 °C) (open circle). b) Temperature dependences (25–150 °C) of lithium ion conductivity of these samples.

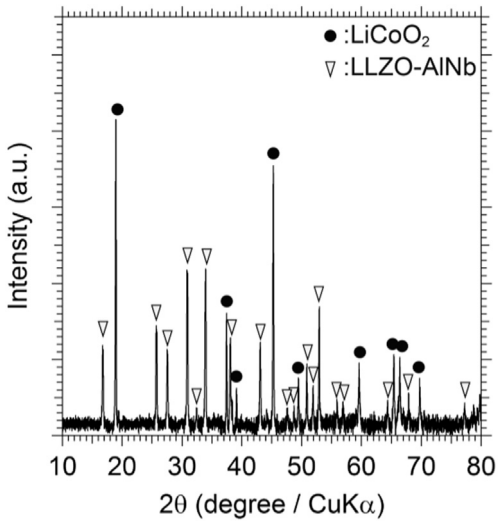

Fig. 6. XRD pattern of co-sintered LLZO-AlNb and LCO.

as that of LLZO-AlNb-conv. (0.4 mS cm^{-1}). In addition, the termination points of the semicircles were 0.7 MHz and 1.0 kHz for R_b and R_{gb}, respectively, for the both samples. These results suggest that the conduction path of Li ions between grains is sufficiently formed for the developed LLZO-AlNb despite of the low sintering temperature (790 °C). Fig. 4b shows temperature dependences of lithium ion conductivity for the developed LLZO-AlNb and LLZO-AlNb-conv. The lithium ion conductivities were linear and obeyed the Arrhenius law ($\sigma = A\exp(-E_a/kT)$, where A is the frequency factor, k is the Boltzmann constant, T is the absolute temperature, and E_a is the activation energy). The E_a for the developed LLZO-AlNb was ~31 kJ mol^{-1}, which is almost the same as that of LLZO-AlNb-conv. and also the reported values [12].

Chemical stability of LLZO-AlNb with LCO during co-sintering was confirmed by focused ion beam scanning electron

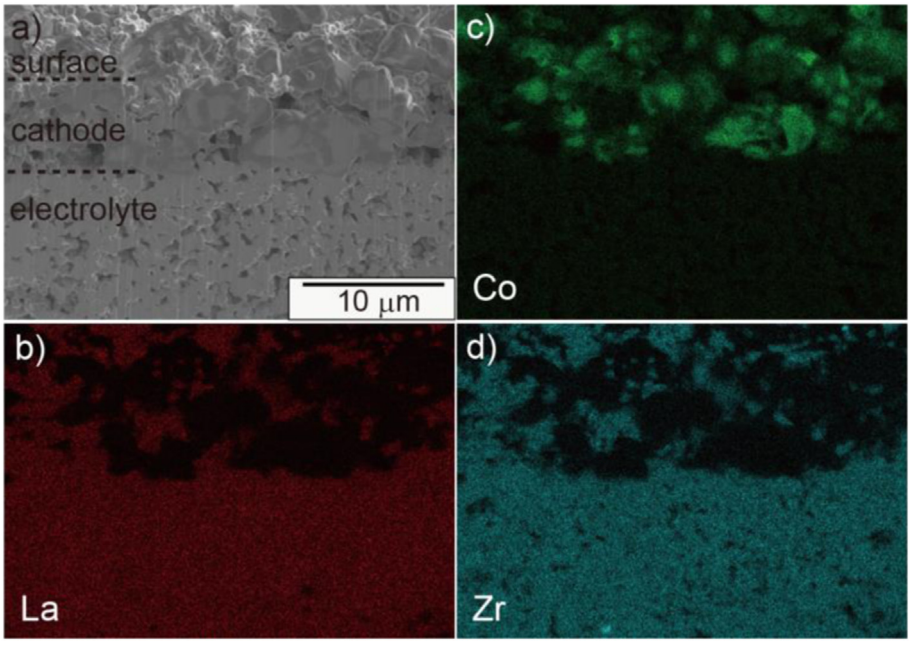

Fig. 5. a) Cross-sectional SEM (secondary electron) image of the cathode/electrolyte interface and EDX mapping images of b) La, c) Co and d) Zr.

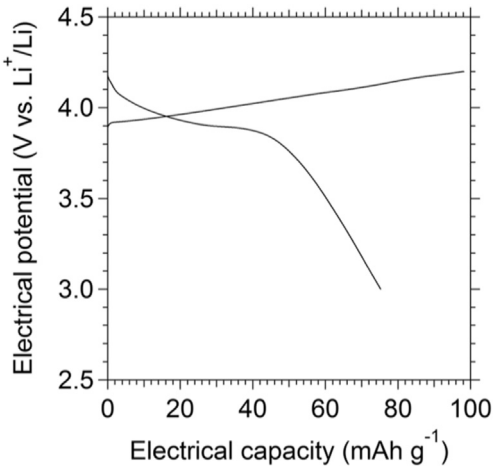

Fig. 7. Charge–discharge curves for the co-sintered model battery. The horizontal axis shows the capacity normalized by the weight of the $LiCoO_2$ cathode.

microscope (FIB-SEM), energy dispersive X-ray analysis (EDX) and XRD. The sample was prepared by stacking of the mixed LCO and LLZO-AlNb cathode layer (thickness: ~10 μm^t) onto the developed LLZO-AlNb electrolyte layer (thickness: ~1.0 mm^t), followed by co-sintering at 790 °C. The cross-sectional SEM image and EDX mapping of the cathode/electrolyte interface is shown in Fig. 5. The interface of LCO grains and LLZO-AlNb grains was primarily well-sintered although a few voids existed. The voids can be formed by capillary action of Li_3BO_3 in the liquid phase to the more porous LLZO-AlNb electrolyte during co-sintering. The EDX mapping confirmed that no elemental diffusion occurred between LCO and LLZO-AlNb. The XRD pattern of the cathode layer showed only diffraction peaks of LCO (JCPDS: 50-0653) and LLZO-AlNb (Fig. 6). These results indicate that no chemical reaction between LCO and LLZO-AlNb occurred at the co-sintering process.

Finally, the developed LLZO-AlNb was confirmed to work well as an electrolyte of an all-solid-state lithium ion battery. The model battery was constructed by coating of Li metal on the electrolyte side of the co-sintered cathode (LLZO-AlNb + LCO)/electrolyte (LLZO-AlNb) pellet, and its battery performance was evaluated. Fig. 7 shows charge–discharge curves of the model battery. The charge curve started at 3.9 V and the plateau of the discharge curve was observed at approximately 3.9 V. These behaviors are typical for the extraction/insertion reaction of LCO and thus the cathode/electrolyte pellet is considered to works properly. However, the charge and discharge capacities of this battery were 98 and 78 mA hg^{-1}, respectively, which correspond to about 72 and 58% of the theoretical capacity [22,23]. In addition, the electrical potential at the end of discharge gradually dropped due to the polarization in cathode layer. These results suggest that the formation of the lithium ion conduction path is not enough in the cathode/electrolyte pellet and thus optimization of the processing (e.g. powder preparation and co-sintering conditions) is necessary to improve the battery performance.

4. Conclusions

We developed a novel lithium garnet-type oxide electrolyte which is densified to 90% in relative density at 790 °C and exhibits a high lithium ion conductivity of 0.36 mS cm^{-1} at 25 °C. Addition of Li_3BO_3 and Al_2O_3 to LLZO-CaNb was found to effectively enhance the sintering by simultaneous interdiffusion of Al and Ca elements between garnet-type oxide and additives. The developed electrolyte was successfully co-sintered with LCO without any reactions between them. The model battery using the developed electrolyte was confirmed to function well as a secondary battery with charge and discharge capacities of 98 and 78 mAh g^{-1}, respectively. These results opened the potential for fabrication of all-solid-state lithium ion batteries using metal oxide electrolytes by a simple and well-established co-sintering process.

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